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THE SECRET OF CERAMIC SPHEROCONES

A. M. Salakhov,[1] G. R. Tuktarova,[1] and V. P. Morozov[1]

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Ceramic spherocones from the site of the ancient settlement of Bolgar (14th century) are investigated. Their strength parameters are compared. The specifics of the mineral compositions of samples are considered.

Among the known varieties of ancient ceramics, archaeologists as early as in the middle of the 19th century became interested in peculiar vessels shaped as a cone with a spherical bottom. Prof. A. Kh. Khalikov, a well-known archaeologist, wrote: “Archeologists studying medieval town culture are familiar with these peculiar vessels; they are found on an extensive territory: in Egypt, Asia Major and Asia Minor, Iran and Central Asia, Transcaucasus, Crimea, and the Volga Region” [1]. Considerable quantities of these vessels have been found in the excavations of the Bilar and Bolgar sites of ancient settlements that at different times used to be the capitals of Volga Bulgaria, which was the first civic formation on the Middle Volga. These settlements are now located in the Alekseevskii and Spasskii districts in the Republic of Tatarstan. The vessels were first subjected to systematic research by A. F. Likhachev, the founder of the Kazan Museum, who in his talk during the 2nd Archeological Congress (1872) put forward a hypothesis that they had been used as icon lamps.

It is surprising that these articles made 800 years ago have been finely preserved and remain intact and undamaged, which can be attributed to their extremely high strength. Several generations of archeologists have asked, which material and what technology had been used and what ceramic artisans had made these objects.

To answer these questions, we have adopted the approach of an engineer-researcher.

We investigated the black and red spherocones that have been well preserved, although their properties differ; ceramic stucco, including dishware, as well as a substantial number of ceramic pipes from the Bolgar settlement of the 14th century. It should be noted that people in ancient Bolgar used pipes of different sizes: diameter 10 – 13 and length 25 – 40 cm. They were produced on a potters’ wheel from well-elutriated paste without visible impurities [2]. The pipe crock fracture is colored red, occasionally with a black core.

In order to estimate the physicomechanical properties of these materials, we determined their hardness, since the small size of these articles prevented estimating their properties by traditional methods.

It was found the hardness of black spherocones is 7 – 8 Mohs, which is significantly higher than in other samples of medieval ceramics (Table 1). Thus the hardness of clay pottery is 4 – 6, ceramic pipes — 6 – 7, and the hardness of brick from the pre-Mongolian period is around 5. Note that a contemporary ordinary brick produced at some brick factories in Kazan or Cheboksary has hardness about 5 as well. It is notable that the black spherocones with respect to their hardness are not inferior to hard porcelain or such contemporary products as ceramogranite or high-grade clinker with compressive strength above 100 MPa.

In the next stage of our research we determined the mineral composition of the products using x-ray phase analysis (Table 1 and Figs. 1 and 2).

It is established that the diffraction patterns of black spherocones differ significantly in their mineral composition from the diffraction patterns of ancient or modern ceramics based on local argillaceous material (Figs. 1*b* – *e* and 2*e*).

The authors have never before met a ceramic material with such a high content of wollastonite ($d = 2.998$ Å, Fig. 1*a*). The very high content (above 15 – 20%) of feldspar is surprising as well ($d = 2.213$ Å). The profile of this diffraction reflection exhibits unresolved maxima of potassium feldspar and plagioclase, which indicates that the firing temperature of these articles is close to the homogenization temperature of the said feldspars. Our experimental data on fir-

[1] Stroitel’naya Keramika Company, Kazan Russia; Kazan State Technological University, Kazan, Russia.

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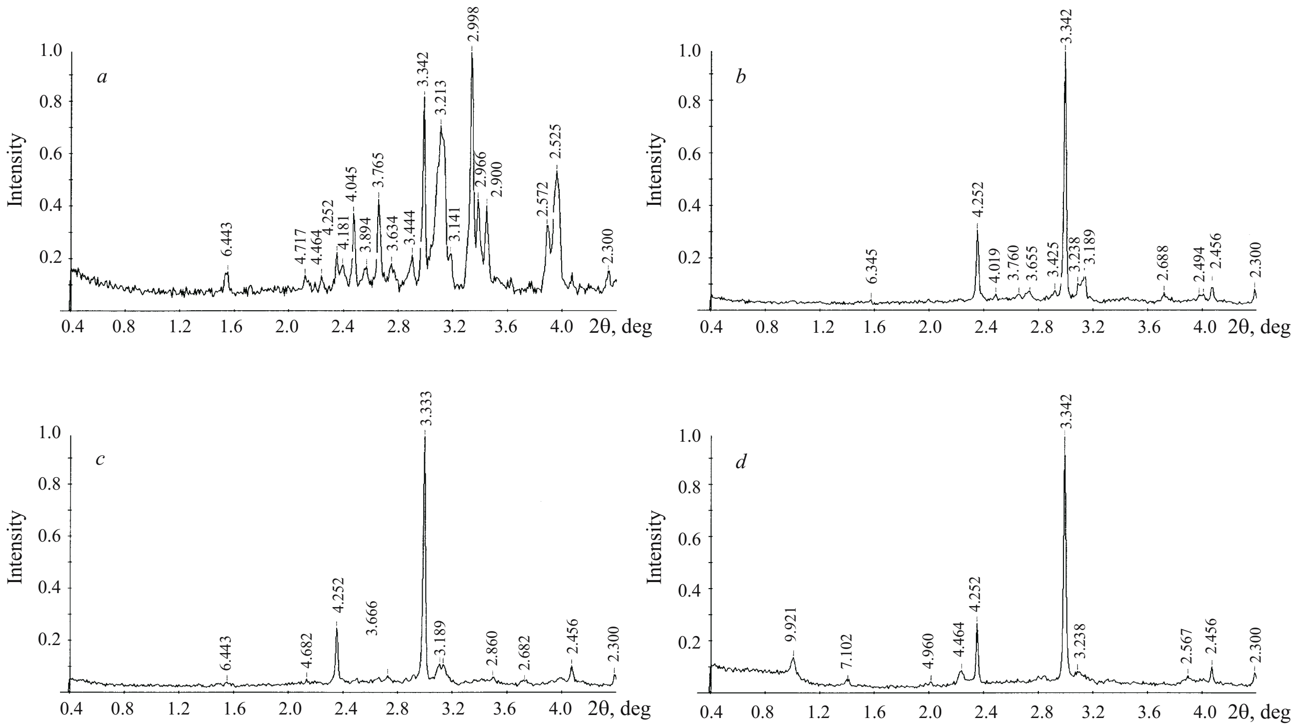

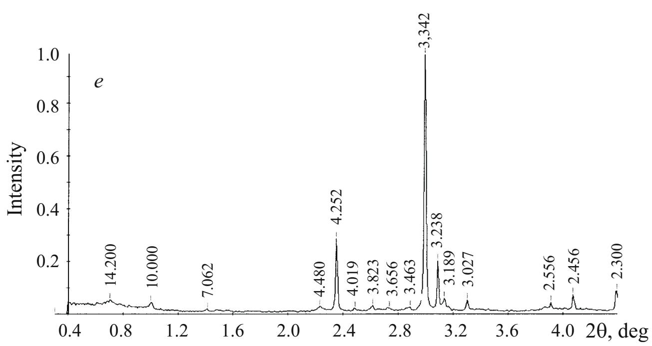

Fig. 1. Diffraction patterns of ancient products: black spherocone from Bilyar settlement (*a*), red-brown spherocone from Bolgar settlement (*b*), water pipe from Bolgar settlement (*c*), ceramic stucco molding from Bolgar settlement (*d*), ceramic brick from Bolgar settlement (*e*).

ing argillaceous materials containing feldspar suggest that the black spherocones were fired at a temperature not less than 1050 – 1100°C.

At the same time, analysis of the diffraction pattern of the black spherocone sample indicates the absence of a clearly defined amorphous glass phase, which is always present in

TABLE 1

Number*	Ancient articles	Moh hardness	Mineral composition	Number*	Modern articles	Mohs hardness	Mineral composition
	Spherocone:						
1a	black color	7 – 8	Wollastonite, quartz, feldspar	2a	Porcelain insulator	7 – 8	Quartz, mullite, amorphous glass phase, cristobalite
1b	red color	5 – 6	Quartz, feldspar,** pyroxenes, hematite	2b	Ceramogranite	~ 8	Quartz, amorphous glass phase, feldspar,** hematite, pyroxenes
1c	Water pipe	6 – 7	Quartz, feldspar,** pyroxenes, hematite, mica	2c	Clinker	~ 8	Quartz, hematite, feldspar,** pyroxene
1d	Stucco molding	4 – 6	Quartz, feldspar,** pyroxene, hematite, mica, chlorite	2d	Facing brick	~ 7	Quartz, feldspar, wollastonite
1e	Brick	~ 5	Quartz, feldspar,** hematite, mica, chlorite	2e	Ordinary brick	< 5	Quartz, feldspar,** pyroxene, hematite

* The number corresponds to the figure number.

** Potassium feldspars + plagioclases.

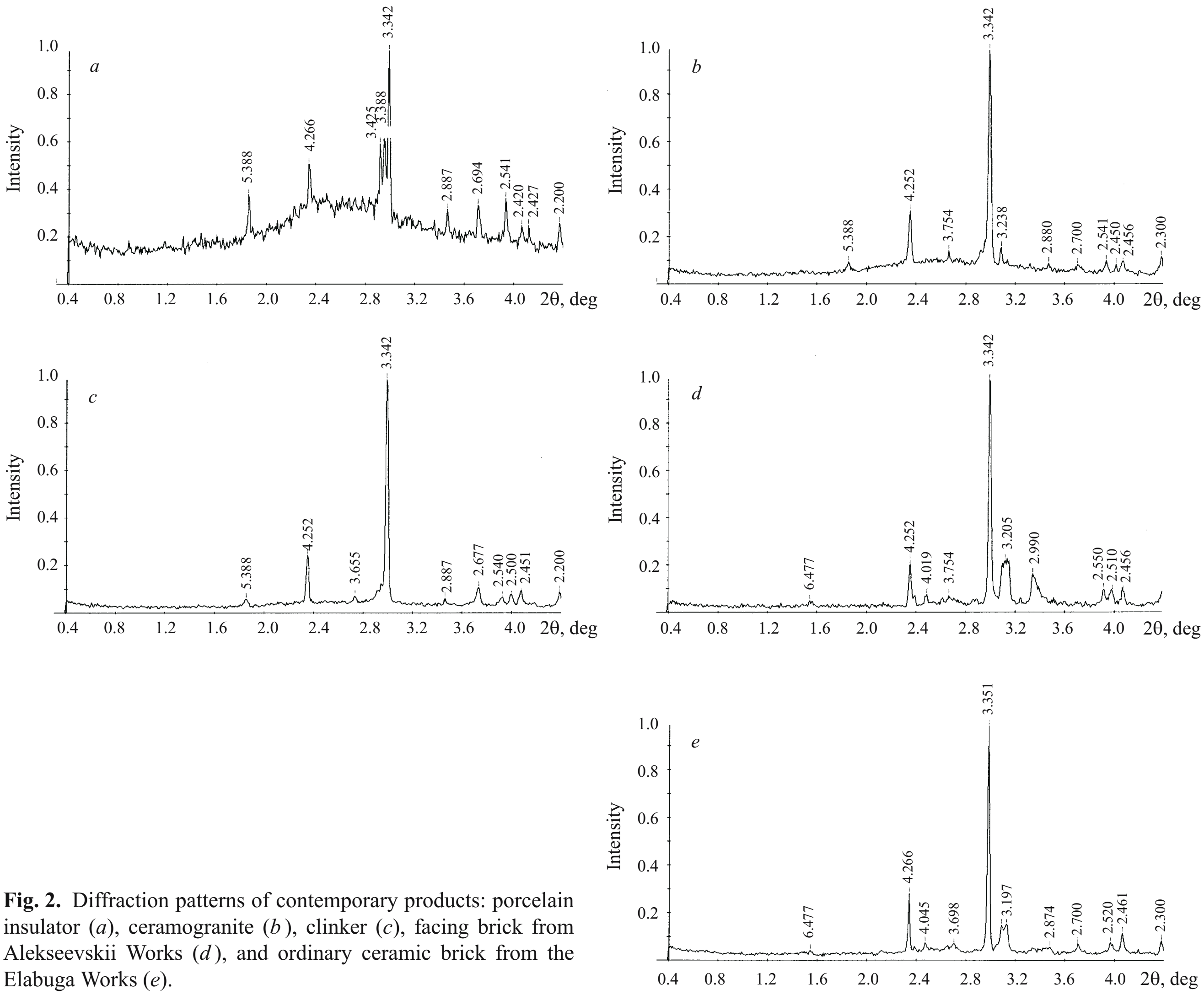

Fig. 2. Diffraction patterns of contemporary products: porcelain insulator (*a*), ceramogranite (*b*), clinker (*c*), facing brick from Alekseevskii Works (*d*), and ordinary ceramic brick from the Elabuga Works (*e*).

the form of an amorphous halo in contemporary high-strength products (Fig. 2*a* and *b*).

It is tempting to imagine that as early as the 12th century the medieval artisans tried to reproduce porcelain, whose secret was discovered in China in the epoch of the Tang dynasty (618 – 907). The production of porcelain especially flourished at the time of the Ming dynasty (1368 – 1644).

It is known [3] that porcelain appeared in Europe only in the 18th century, initially just soft porcelain, and hard porcelain appeared only in the 19th century. The diffraction patterns of hard porcelain obtained by us exhibit a significant difference between these two materials. First, the diffraction pattern of a porcelain insulator has a substantial quantity of the amorphous glass phase, which is responsible not only for its hardness but also for its color and translucence.

Moreover, mullite is necessarily identified on the diffraction pattern of porcelain, whereas our numerous studies established that mullite is not present in the composition of ceramic spherocones. This suggests the following conclusion: the common belief in a correlation between the strength (hardness) of ceramics and the formation of mullite is erroneous. Furthermore, our experiments have established that mullite is indeed formed in kaolinite in firing. However, the fired samples do not possess strength. The authors have carried out extensive analysis of different ceramic materials, both ancient and modern. It is impossible to establish any correlation between the strength and durability of the materials and the presence or absence of mullite. On the contrary, several types of construction ceramics that do not contain mullite have better strength parameters than some products containing mullite. Examples of the former are, for instance, clinker and ceramogranite (Table 1).

X-ray phase analysis of clinker or ceramogranite, which is a commonly used material, corroborates the absence of mullite.

It has been noted that the main peculiarity of the mineral composition of the black spherocones is their significant content of wollastonite (above 10 – 15%).

It is known [4, 5] that wollastonite is formed in the products of joint firing of polymineral red-burning clays and

calcite. Our study of the facing brick from the Alekseevskaya Keramika Company, which is produced using quaternary red-burning clays and marl, corroborated this fact as well. Moreover, we have identified wollastonite in the brick of the 18th century used to build the Semioserskii monastery near Kazan. As was justly said by Prof. A. A. Khalikov [1], starting with ancient times, carbonates in the western regions of Central Asia were used as grog components and decreased the shrinkage of vessels in drying and firing.

In 1985 the archaeological excavations of the ancient settlement of Bulgar discovered as well fragments of different thick-walled spherocones with a red-color fracture. Their diffraction pattern (Fig. 1*b*) indicates that their main minerals are quartz, feldspar (to a significantly less extent than in black spherocones), and x-ray-amorphous argillaceous mineral relicts. The obtained diffraction patterns are virtually identical to the diffraction patterns of modern ceramics made from local argillaceous material that forms the basis for the contemporary production of ceramics, bricks, and pottery in Kazan, Elabuga, Nizhnekamsk, and other cities of the Republic of Tatarstan. The ancient and contemporary materials have very similar strength parameters.

All spherocones found in Bilyar and Bolgar were made using a potter's wheel. Many of them are covered on the outside by a thin engobe coating. Nearly all spherocones have some kind of ornamentation in the upper part.

The question of black spherocone firing site and method remain extremely interesting, but not yet clarified. It is clear that we are dealing with one of the earliest composite materials in Europe. Analysis of the literature and the authors' own data show that none of the known materials can produce auricles with the same qualitative and quantitative composition as that of black spherocones. The absence of an amorphous glass phase in the fired products shows that the temperature of spherocone firing has to be no higher than 1100°C (this is supported by the homogenization of potassium feldspar and plagioclase), but yet below the firing temperature of soft porcelain (1250°C). Mullite, which is the product of thermal dissociation of kaolinite in the production of porcelain, has not been identified in the spherocone either [6]. Consequently, kaolinite clay was not used in the production of spherocones.

Thus, deciphering the mineral composition of black spherocones suggests the following hypothesis: these articles were made from a composite batch. It probably included red-burning clay, calcite (it could be either milled limestone (marble), or calcareous marl), and milled feldspar. Such three-component batch in firing yields a mineral composition equivalent to the composition of black spherocones.

Furthermore, our hypothesis is based on knowledge of local minerals in the Republic of Tatarstan. While red-burning clay and limestone are common local materials and calcareous marl as well is frequently found on the territory of the republic, Tatarstan has no feldspar deposits. Consequently, the considered products were imported to the ancient settlements on the territory of Tatarstan and their production technology was very close to the porcelain production technology.

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